

Coulomb Correlations and Magnetic Anisotropy in ordered $L1_0$ CoPt and FePt alloys

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We present results of the magneto-crystalline anisotropy energy (MAE) calculations for chemically ordered $L1_0$ CoPt and FePt alloys taking into account the effects of strong electronic correlations and spin-orbit coupling. The local spin density + Hubbard U approximation (LSDA+U) is shown to provide a consistent picture of the magnetic ground state properties when intra-atomic Coulomb correlations are included for both $3d$ and $5d$ elements. Our results demonstrate significant and complex contribution of correlation effects to large MAE of these material.

Recent progress in fabrication and characterization of the magnetic nano-particles and thin films based on the ordered $L1_0$ CoPt and FePt alloys renewed interest in understanding the mechanisms contributing to the large magneto-crystalline anisotropy of these materials. While the earlier studies were primarily motivated by permanent magnet applications, current research efforts are focused on the use of CoPt and FePt alloys for the high density magnetic recording. The large and controllable magnetic anisotropy energy (MAE) is then a crucial property to overcome a superparamagnetic limit [1].

The chemically ordered $L1_0$ phase of FePt has large uniaxial MAE ($\approx 6.6 * 10^7 \text{erg/cc}$) which is almost by two orders of magnitude higher than their disordered fcc phase (a dramatic MAE increase with chemical ordering is also typical for other alloys of this kind: CoPt and FePd). The cubic symmetry is broken in $L1_0$ phase by (i) stacking of alternate planes of $3d$ element (Fe or Co) and Pt along [001] direction; (ii) by tetragonal distortion due to $3d$ and $5d$ atomic size mismatch. For the tetragonal crystal with uniaxial symmetry, the MAE depends on polar θ magnetization angle [2] as,

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad (1)$$

where K_1 and K_2 are the anisotropy constants. The series Eq.(1) is rapidly converging and $K_1 \gg K_2$ for CoPt and FePt $L1_0$ alloys [3, 4]. The MAE is then computed as the total energy difference when magnetization is oriented along [110] and [001] crystal axes ($\text{MAE} = E[110] - E[001]$).

A significant amount of work has been done to calculate this energy difference from first principles, employing the local spin density approximation (LSDA). For the case of CoPt alloy, the fully relativistic Korringa-Kohn-Rostoker (KKR) method yields the MAE of 0.058 meV/f.u. which is very different from results of linear muffin-tin orbitals method (LMTO) calculations in atomic-sphere-approximation (ASA): 2.29 meV [6], 1.5 meV [7], 2 meV [8], the augmented-spherical-wave (ASW) result of 0.97 meV [9], and full-potential LMTO (FLMTO) calculation results of 1.05 meV [10] and 2.2 meV [11]. As can be seen, there is an apparent and

significant scatter of the theoretical results, while the experimental measurements are known to be quite accurate and consistent yielding the MAE of 1 meV [3]. The situation is similar for the case of FePt alloy: the LMTO-ASA calculations yield 3.4 meV [6], 2.8 meV [7], 3.5 meV [8], ASW yields [9] 2.75 meV, and FLMTO 3.9 meV [11] and 2.7 meV [10], and none of these calculations reproduce the experimental MAE of 1.3 – 1.4 meV for the bulk [4], and 1 – 1.2 meV for the films [12] (when extrapolated to $T=0$ [13]).

The accurate *ab-initio* calculation of the MAE in itinerant ferromagnet is a very difficult task due to its notorious sensitivity to numerical details [14]. More importantly, the LSDA (or generalized gradient approximation (GGA)) which is conventionally used in the first-principles theory, lacks proper orbital polarization due to Coulomb correlation effects [15]. In this paper, we wish (i) to clarify the ability of the LSDA theory to reproduce the experimental MAE for CoPt and FePt alloys, when highly accurate full-potential relativistic linearized augmented plane wave method (FP-LAPW) is used for the total energy MAE calculations; (ii) to go beyond LSDA and to investigate the role of electron correlations. We account for the on-site Coulomb correlation effects by using the LSDA+U approach [16] and to show that correlations should be included for both “magnetic” (Fe and Co) and “non-magnetic” (Pt) sites to describe consistently the magnetic ground state properties, such as the MAE and spin and orbital magnetic moments. For the first time, we quantitatively demonstrate a significant and complex character of the intra-atomic Coulomb repulsion contribution to the MAE of itinerant ferromagnet with strongly magnetic $3d$ and non-magnetic $5d$ -elements.

We start with the conventional LSDA band theoretical method together with the relativistic FP-LAPW method [17] and apply them to perform total energy electronic and magnetic structure calculations for the magnetization fixed along each of [110] and [001] axes, respectively and the MAE. The special k -points method is used for Brillouin Zone integration with the Gaussian smearing of 1 mRy for k -points weighting [14]. For convergence of the total energy differences within desired accuracy (bet-

TABLE I: Magnetic Anisotropy Energy (meV/f.u.) calculated using FP-LAPW method within the LSDA theory.

	Ref. [9]	Ref. [11]	Ref. [10]	Present
CoPt	0.97	2.2	1.05	1.03
Exp.	0.82 ($T = 293$ K) [3]; 1.00 ($T = 0$ K) [13]			
FePt	2.75	3.9	2.73	2.68
Exp.	0.7 – 1.2 ($T = 293$ K) [4, 12]; 1 – 1.4 ($T = 0$ K) [13]			

ter than a few μeV), about 11000 k -points are used (the MAE as a function of k -points number is calculated to be very similar to the results of Ref. [10]). The experimental values for the lattice parameters ($a = 7.19$ a.u., $c = 7.01$ a.u. for CoPt, and $a = 7.30$ a.u., $c = 7.15$ a.u. for FePt) are used [10]. The calculated MAE is shown in Table I. in comparison with recent total energy calculations and experimental results. The present FP-LAPW results are in very good quantitative agreement with ASW results of Oppeneer [9] and FLMTO results of Ravindran [10] and disagree substantially with FLMTO results of Galanakis [11] for the reason which is unclear to us. For CoPt alloy the MAE is calculated in a very good agreement with experimental data, while for FePt our LSDA results (together with those of Refs. [9, 10]) overestimate value of MAE by a factor of two.

Very recently, the electron-electron interaction was shown to play an important role for the MAE in itinerant d [18] and f -electron [19] magnetic materials. Here, we use the LSDA+ U method combined with relativistic FP-LAPW basis [19, 20] to account for the intra-site Coulomb repulsion U . Minimization of the LSDA+ U total energy functional with SOC treated self-consistently [17] generates not only the ground state energy but also one-electron energies and states providing the orbital contribution to the magnetic moment. The basic difference of LSDA+ U calculations from the LSDA is its explicit dependence on on-site spin and orbitally resolved occupation matrices. The LSDA+ U creates in addition to spin-only dependent LSDA potential, the spin and orbitally dependent on-site “+ U ” potential which produces the orbital polarization [21]. Since the LSDA+ U method is rarely applied to metals, the appropriate values of intra-atomic repulsion U for Fe, Co and Pt atoms in metals are not known precisely as they are strongly affected by the metallic screening. Here we choose U_{3d} from the range of 1-2 eV, and U_{5d} from the range of 0-1 eV (according to the experimental values for pure metals [22]) in order to reproduce experimental values of the MAE. For the exchange J we use the values of $J_{Co} = 0.911$ eV, $J_{Fe} = 0.844$ eV, $J_{Pt} = 0.544$ eV which are obtained as a result of constrained LSDA calculations [23], and are close to their atomic values.

First, we discuss the FePt alloy. The MAE as a function of U_{Fe} is shown in Fig. 1(a). When U is included on Fe-site only and varied in the interval of 1-2 eV, the MAE is decreasing from its LSDA value. The experi-

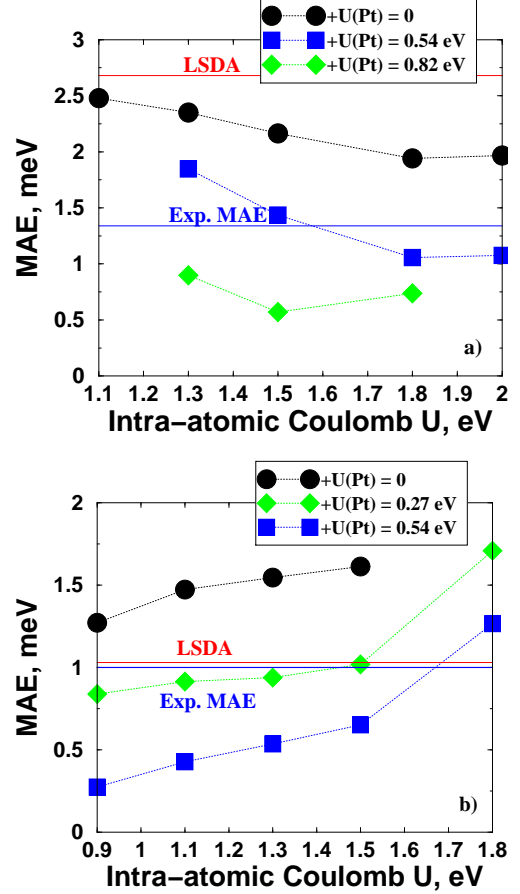


FIG. 1: (color) The MAE vs intra-atomic Coulomb repulsion (U) on 3d-site for (a) FePt alloy; (b) CoPt alloy for different values of U on Pt-site. Note, that we use the bulk experimental MAE values [3, 4] extrapolated to $T = 0$ K.

mental value of the MAE can not be reached without unreasonable increase of U . Further meaningful reduction of the MAE can be achieved by including U on the Pt-site (see, Fig. 1(a)) and for the value of U_{Pt} around 0.544 eV ($= J_{Pt}$) the MAE observed for the bulk FePt can be reproduced. We note that the correct value of the MAE can be obtained in the region of $U_{Fe} \approx 1.5$ -1.6 eV, $U_{Pt} \approx 0.5$ -0.6 eV.

We choose the $\{U_{Fe} = 1.516$ eV, $U_{Pt} = 0.544$ eV $\}$ as a representative material specific parameters set to analyze the spin and orbital ground state properties. The calculated spin M_s , orbital M_l and total magnetic moments for the magnetization directed along [001] axis are shown in Table II. The LSDA+ U agrees with observed total magnetization/f.u. M^{tot} , yields a slight increase of M_s^{Fe} from its LSDA value of $2.88 \mu_B$ and substantially increases the M_l^{Fe} from $0.0657 \mu_B$. The change of M_s and M_l of Pt-site is very small as compared with LSDA. The effect of U on the M_l is seen to be similar to the “orbital polarization correction” of Brooks *et al.* (LSDA+OP) [10] (see, Table II). This *ad-hoc* LSDA+OP

TABLE II: Spin (M_s), Orbital (M_l) magnetic moments for 3d and 5d atoms, and Total Magnetic Moment (M^{tot}) per formula unit (μ_B); Magnetic Anisotropy Energy (meV/f.u.) as results of LSDA+U calculations for FePt and CoPt alloys. The LSDA+U calculated M_s and M_l values for bcc-Fe and hcp-Co obtained with the same values for U_{3d} and J_{3d} as for Fe- and Co-atoms in FePt and CoPt alloys.

FePt[001]	MAE	M^{tot}	Atom	M_s	M_l
LSDA+U	1.3	3.47	Fe	3.00	0.114
{ $U_{Fe} = 1.52$ eV, $U_{Pt} = 0.54$ eV}			Pt	0.34	0.048
LSDA+OP	2.9	3.36	Fe	2.89	0.110
			Pt	0.35	0.048
Exp.	1.3	3.4			
CoPt[001]	MAE	M^{tot}	Atom	M_s	M_l
LSDA+U	1.0	2.55	Co	1.93	0.253
{ $U_{Co} = 1.70$ eV, $U_{Pt} = 0.54$ eV}			Pt	0.38	0.065
LSDA+OP	1.64	2.37	Co	1.80	0.161
			Pt	0.39	0.062
Exp.	1.0	2.4	Co	1.9-2.1	0.284
			Pt	0.36	0.090
bcc-Fe[001]				M_s	M_l
LSDA+U	$U_{Fe} = 1.52$ eV			2.234	0.085
LSDA+OP [14]				2.193	0.078
Exp.				2.13	0.08
hcp-Co[0001]				M_s	M_l
LSDA+U	$U_{Co} = 1.70$ eV			1.631	0.153
LSDA+OP [14]				1.591	0.123
Exp.				1.52	0.14

correction is known to improve the M_l in a number of d - and f -electron compounds, but it does not reproduce the MAE for FePt alloy.

We now describe CoPt alloy. The MAE as a function of U_{Co} is shown in Fig. 1(b). When U is included on Co-site only and varied in the interval of 1-2 eV, the MAE increases from its LSDA value and deviates from the experiment. As in the case of FePt alloy, we need to include U on the Pt-site. The increase of U_{Pt} yields the decrease of the MAE and its correct value is found in the region of $\{U_{Co} \approx 1.4-1.7$ eV, $U_{Pt} \approx 0.3-0.6$ eV}. We choose the set $\{U_{Co} = 1.698$ eV, $U_{Pt} = 0.544$ eV} as a representative (note, that we use the same value of U_{Pt} as for the FePt alloy, indicating its transferability). The calculated ground state M_s , M_l and M^{tot} for the magnetization directed along [001] axis are shown in Table II. The M^{tot} is calculated in a good quantitative agreement with results of LSDA+OP and experimental data [8]. There is only small increase in M_s^{Co} from LSDA value of $1.81 \mu_B$ while the M_l^{Co} is substantially enhanced from its LSDA value of $0.093 \mu_B$ (Table II). The change of M_s and M_l for Pt-site is very small. The M_l^{Co} increase in LSDA+U calculations is substantially more pronounced than obtained in LSDA+OP approximation [10].

Recently, the element-specific M_s and M_l for CoPt were measured by Grange *et al.* using the X-ray Magnetic Circular Dichroism (XMCD) [24]. The LSDA+U calculated values for M_s and M_l for the Co-site are in

a good quantitative agreement with XMCD results [25]. For the Pt-site, the agreement is not as good. Probably it is caused by the use of the atomic-like sum rules to extract M_s and M_l from XMCD spectra. This procedure is not reliable for Pt due to substantially itinerant character of Pt 5d-electrons. The LSDA+U calculations reproduce consistently the MAE, total, spin and orbital ground state magnetic moments for CoPt alloy (Table II). Both LSDA and LSDA+OP are only partially successful: LSDA yields correct value of MAE but fails for M_l^{Co} and LSDA+OP improves somewhat M_l but does not reproduce the MAE.

To evaluate further the consistency of the LSDA+U results, we performed the LSDA+U calculations for the elemental 3d-ferromagnet bcc-Fe and hcp-Co with the same values of the U_{3d} and J_{3d} as for Fe- and Co-atoms in FePt and CoPt alloys (see, Table II). It is seen that without any further adjustments of parameters the LSDA+U provides very reasonable results for the orbital magnetization in elemental 3d ferromagnet. These results demonstrate that the on-site Coulomb interaction parameters U_{3d} are well transferable in the transitional d -metal systems.

As for the choice of the Coulomb- U for Pt, the challenge lies in correcting the LSDA orbital polarization without harming the exchange splitting which is expected to be well accounted in the LSDA. The choice of $U_{Pt} = 0.5-0.6$ eV looks then quite reasonable. Indeed, for the Pt-5d states having almost equal on-site occupations, the choice of $U_{Pt} \approx J_{Pt}$ corresponds to an effective Stoner exchange $I_{LSDA+U} \approx I_{LSDA}$ [29] preserving the LSDA spin polarization. This allows to ensure that the LSDA+U correction contributes entirely to the orbital polarization. The LSDA+U method, while proposed to deal with the problems specific for the localized states, in fact is not limited by this case. This method can be used as soon as on-site Coulomb correlation in the form of the Hubbard model is physically meaningful. The above comparison with available experimental data for the MAE and spin/orbital magnetic moments, and physically reasonable choice of parameters justify the use of on-site LSDA+U correction [16] for the Pt-5d states as the way to correct on-site orbital polarization.

We now discuss the relation between the MAE and the anisotropy of the orbital magnetic moment $\Delta M_l (= M_l \parallel [110] - M_l \parallel [001])$. Bruno [26] showed that in the limit of strong exchange splitting $\Delta_{ex} \gg \text{SOC}$, the MAE is proportional to ΔM_l . This model predicts the positive MAE of 0.2 meV for CoPt and negative MAE of -2.1 meV for FePt, in disagreement with the total energy calculations and experiment (Table II).

A more general form for MAE was given in Ref. [27]:

$$\text{MAE} \approx -\frac{\xi}{4} \Delta(M_l^\downarrow - M_l^\uparrow) + \Delta E_T[\uparrow\downarrow - \text{“spin-flip”}] \quad (2)$$

where ξ is the SOC constant. The 1st term (ΔE_L) is the

$\uparrow\uparrow; \downarrow\downarrow$ -spins contribution due to the orbital moment \vec{L} , and the 2nd term couples the $\uparrow\downarrow$ -spins and is related to the spin magnetic dipole moment \vec{T} . In the limit of SOC $\ll \Delta_{ex}$, the $\Delta E_T \approx -3\xi^2/\Delta_{ex}[\Delta Q_{zz}]$ is proportional to the difference of quadrupole moments Q_{zz} for $z = [110], [001]$. Note, that this ΔE_T form is valid for Fe and Co since their SOC (0.07-0.08 eV) $\ll \Delta_{ex}$ (3-4 eV) and can not be used for Pt which has the SOC (0.6 eV) $> \Delta_{ex}$ (0.2 eV) [28].

The Eq.(2) gives for the CoPt alloy $\Delta E_L^{Co}=1.4$ meV, $\Delta E_T^{Co}=-0.7$ meV and $\Delta E_L^{Pt}=1.9$ meV, and for FePt alloy, $\Delta E_L^{Fe}=-0.1$ meV, $\Delta E_T^{Fe}=1.0$ meV, and $\Delta E_L^{Pt}=1.2$ meV. Here, large $\Delta E_T^{Fe,Co}$ contributions to the MAE naturally originate from the difference in the inter-plane $\{xz, yz\}$ $3d-5d$ and in-plane $\{xy\}$ $3d-3d$ hybridization. Without ΔE_T^{Pt} contribution, the total MAE of 2.7 meV (CoPt) and 2.1 meV (FePt) can be estimated, exceeding substantially the experimental values (cf., Table II). We can only roughly estimate that $\Delta E_T^{Pt} \sim -\Delta Q_{zz} (= 0.12$ (CoPt), 0.09 (FePt)) provides additional negative MAE contributions which are expected to reduce a total MAE towards the experimental data. Thus, due to the strong Pt-SOC, neither of commonly used MAE parameterizations [26, 27] based on SOC-perturbation theory expansions is valid on the quantitative and do not provide a substitute for the total energy MAE calculations.

Still, it is of interest to apply the Eq. (2) to analyze qualitatively the origin of MAE dependence on U shown in Fig.1. This analysis shows that LSDA+U MAE vs U dependence is qualitatively consistent with the Eq.(2), and the change in $\Delta E_L^{Pt} \sim \Delta(M_l^\downarrow - M_l^\uparrow)^{Pt}$ contributes substantially to the MAE variations with the U . In particular, we find the ‘‘coupling’’ between U_{3d} and ΔE_L^{Pt} which originates from strong $3d-5d$ hybridization, so that tiny U_{3d} -induced changes in Pt- $\Delta(M_l^\downarrow - M_l^\uparrow)$ produce substantial MAE change due to the strong Pt-SOC. It also explains surprisingly strong MAE dependence on U_{Pt} (cf., Fig.1), as a variation of U_{Pt} causes tiny Pt- $\Delta(M_l^\downarrow - M_l^\uparrow)$ change ($\sim 10^{-3} \mu_B$) which in turn changes the MAE substantially due to the strong Pt-SOC.

To summarize, accounting for on-site Coulomb correlations beyond what is included in LSDA, and using the LSDA+U method in a very general implementation including SOC we have provided a microscopic theory of the ground state magnetic properties in $L1_0$ FePt and CoPt alloys. It is shown by comparison with the experiment that LSDA+U method is capable of describing quantitatively the MAE and orbital magnetization in these alloys with physically reasonable choice of Coulomb- U parameters. Using the SOC-perturbation theory model we provide interpretation of our numerical results. These results are believed to be important for quantitative microscopic understanding of the large MAE in these material, and will assist in the develop-

ment of the next generation magnetic recording devices operating above $Tbit/in^2$ recording densities.

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